



Short communication

One-step synthesis of high performance $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6\text{--}\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite cathode for intermediate-temperature solid oxide fuel cells using a self-combustion technique

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H I G H L I G H T S

- ▶ A one-step self-combustion method is proposed to prepare SFMO–SDC composite.
- ▶ The SFMO–SDC cathode shows porous nanostructure and uniform elements distribution.
- ▶ High performance of SFMO–SDC cathode is presented by low polarization resistance.
- ▶ The maximum power densities reach 2.21, 1.66 and 1.16 W cm^{−2} at 800, 750 and 700 °C.

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A $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6\text{--}\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SFMO–SDC) nanocomposite material has been prepared by the self-combustion method. The phase structure and morphology of the material have been characterized by means of X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). These results show the coexistence of perovskite and fluorite structures within the porous microstructure which are uniformly distributed throughout the prepared samples. The electrochemical performance of the material has been investigated by electrochemical impedance spectroscopy (EIS) measurements. Using an SDC interlayer SFMO–SDC composite cathode is prepared and applied onto a standard YSZ (8% Y_2O_3 -stabilized ZrO_2) electrolyte. A low polarization resistance of the prepared sample is obtained and remarkable performance of the SFMO–SDC based IT-SOFCs is achieved. It is demonstrated that the SFMO–SDC/SDC/YSZ/NiO–YSZ fuel cell reached power densities of 2.21, 1.66, 1.16 and 0.71 W cm^{−2} at 800, 750, 700 and 650 °C, respectively, in humidified H_2 (3 vol% H_2O).

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion devices that generate electric power through electrochemical reactions between an oxidant and a fuel gas, for example air and hydrogen [1,2]. Intermediate temperature SOFCs (IT-SOFCs) operating at 600–800 °C are expected to reduce the cost of the SOFC manufacture while sustaining reasonably rapid kinetics for the electrochemical reactions in the electrodes [3,4]. However, the use of traditional cathode materials in IT-SOFC manufacture demonstrates poor activity for the oxygen reduction reaction (ORR). Current efforts therefore focus on either exploring advanced electrode materials or optimizing the cathode microstructure by using novel strategies. Irvine et al., for example, reported an efficient

SOFC based upon single-phase perovskites which minimized the polarization losses across the electrolyte/electrode interface [5]. In another example, a three-dimensional fibrous cathode was fabricated for high-performance SOFC operating at low temperatures [6]. Alternatively, composite cathodes could be an effective strategy to improve the electrochemical performance of IT-SOFCs. Compared with single-phase cathodes, a higher ORR activity may be achieved using composite materials, with the extra phase enhancing the electronic or ionic conductivity [7–9]. Generally, the fabrication of composite cathodes is based on mechanical mixing of different phases or by an impregnation technique. For example Murray et al. investigated $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3\text{--}\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (LSCF–GDC) composite cathode prepared by mechanical mixing of different phases [10] whereas LSCF–YSZ (Y_2O_3 -stabilized ZrO_2) composite cathode was fabricated by impregnating LSCF nitrate solution into a pre-sintered porous YSZ scaffold [11]. Both methods were observed to significantly enhance the LSCF cathode

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performance. However these traditional methods usually require multiple steps and are time-consuming. Thus, a facile method to fabricate high performed IT-SOFC composite cathodes is highly desired.

Recently, a mixed-conductive perovskite material namely $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6$ (SFMO) was reported as both cathode and anode materials in IT-SOFCs. The performance of the SFMO based fuel cells was investigated by utilizing $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.87}\text{Mg}_{0.13}\text{O}_3$ (LSGM) as the electrolyte [12–15]. SFMO was demonstrated to be a good electrode material for SOFC, showing excellent redox stability and remarkable electrical conductivity in both oxidizing and reducing environments.

In this work, we propose a novel strategy to prepare the $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_6\text{--Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SFMO–SDC) composite cathode for IT-SOFCs by a facile self-combustion technology. This strategy can produce a nanocomposite material with homogeneously distributed SFMO and SDC phases. Furthermore, the SFMO–SDC material possesses a uniform porous nanostructure and stable electrochemical performance. Up to now, the practical applications of SFMO combined with traditional YSZ (8% Y_2O_3 -stabilized ZrO_2) electrolyte has been problematic as it is known that a chemical reaction between the SFMO and YSZ occurs after firing at 1000 °C for 24 h in air [12]. In order to solve this problem, a nanoporous $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) interlayer has been introduced between the YSZ and cathode in our investigation. The single cell performance of this IT-SOFC using the SFMO–SDC cathode and a NiO–YSZ anode supported YSZ electrolyte film has been determined.

2. Experimental

2.1. Materials preparation

SFMO–SDC (60:40 wt%) composite powders were synthesized by a one-step self-combustion method. Stoichiometric amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{N}-\text{O}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as the metal precursors. Glycine and citric acid were used to assist combustion. The mole ratio of glycine and citric acid to the total metal cations was 1.8. A yellowish solution was obtained which was subsequently dried at 80 °C to form a transparent gel. The resulting gel was further heated at 250 °C until the composite gel self-combusted. The ash from this was then calcined at 800 °C for 2 h and at 1000 °C for 5 h in air to obtain an SFMO–SDC composite powder. Both SFMO and SDC powders were obtained by self-combustion technology for study in this investigation.

2.2. Fabrication of SOFCs with SFMO–SDC cathodes

The SFMO–SDC cathode performance was studied by assembling a single cell. Here a NiO–YSZ anode supported YSZ electrolyte film was prepared by standard co-tape casting technology [16]. An SDC interlayer was screen-printed onto the electrolyte and then sintered at 1400 °C for 6 h. The SFMO–SDC composite cathode was then screen-printed onto the SDC interlayer and calcinated at 1000 °C for 2 h.

2.3. Characteristics of SFMO–SDC cathode

The phase structure of the composite cathode was determined by XRD (X' Pert PRO MPD). The microstructure of the composite powder and the prepared electrode was observed using a scanning electron microscope (SEM, FEI QUANTA-250). The thermal expansion coefficient (TEC) was measured using a dilatometer (Netsch DIL 402C) from 40 °C to 900 °C. The three-electrode cell which was fabricated for electrochemical impedance spectroscopy (EIS)

measurements has been described previously [17]. The cells were tested with humidified hydrogen (3 vol% H_2O) at a flow rate of 50 mL min^{-1} and ambient air as the oxidant. The current–voltage curves of the cells were recorded using an Arbin Instruments (Fuel Cell Test System, FCTS).

3. Results and discussion

3.1. Phase structure and microstructure of SFMO–SDC cathode

The phase structure of the prepared SFMO–SDC nanocomposites was investigated by XRD. Fig. 1 depicts the XRD patterns of SFMO, SDC, and SFMO–SDC powders. Here it can be seen that the corresponding peaks of SFMO and SDC are clearly presented in the SFMO–SDC samples and no impurity phases can be observed. This result indicates that the SFMO–SDC composite oxides were successfully obtained and there was no further chemical reaction between SFMO and SDC during the preparation process. This result strongly suggests that self-combustion is an effective way to prepare such SFMO–SDC composite samples.

Fig. 2a shows the micrograph of the SFMO–SDC composite powder observed by SEM. It can be seen that the SFMO–SDC displays a porous structure with a layered network containing interconnecting pores. It is believed that such a structure is favorable for gas diffusion and/or ion/electron conduction when the SFMO–SDC oxide powders are used as the cathode in IT-SOFCs. In addition, as shown in Fig. 2a inset, this powder is composed of SFMO and SDC nanoparticles, which should provide more triple phase boundaries (TPB) during the electrode reaction. The corresponding EDX mappings of the SFMO–SDC composite oxides are also given in Fig. 2b. The homogeneous distribution for Fe, Sr, Mo, Ce and Sm elements is well defined within these images. These results further confirm that SFMO and SDC are uniformly distributed in the oxide composite by using the one step self-combustion method.

In accordance with Section 2.2 single cells of SFMO–SDC/SDC/YSZ/NiO–YSZ were fabricated. Fig. 3a depicts the cross-section SEM image of the resulting cell with the SFMO–SDC cathode including an approximate 10 μm YSZ film acting as an electrolyte and a 700–800 μm thick NiO–YSZ anode. The SFMO–SDC cathode is about 14 μm thick (Fig. 3a). Fig. 3b shows the surface image of the SFMO–SDC composite cathode. Here the porous and layered microstructure of the SFMO–SDC powder (Fig. 2a) is clearly observed demonstrating that it is successfully maintained even after sintering at 1000 °C for 2 h. This result implies that the calcination

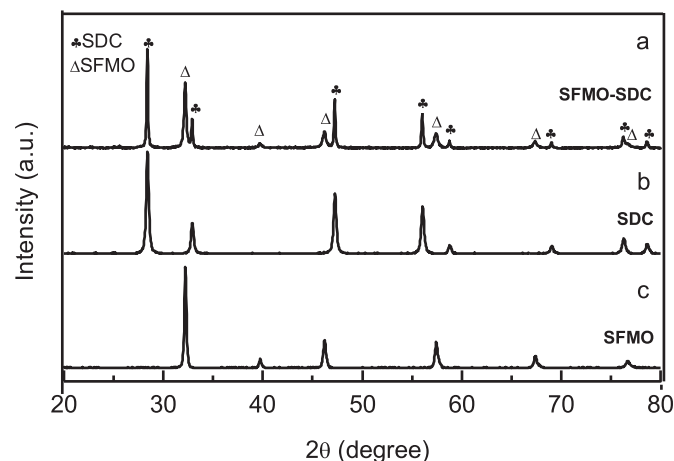


Fig. 1. XRD patterns of (a) the composite oxide of SFMO–SDC (60:40 wt%) fired at 800 °C for 2 h and 1000 °C for 5 h in air, (b) SDC and (c) SFMO.

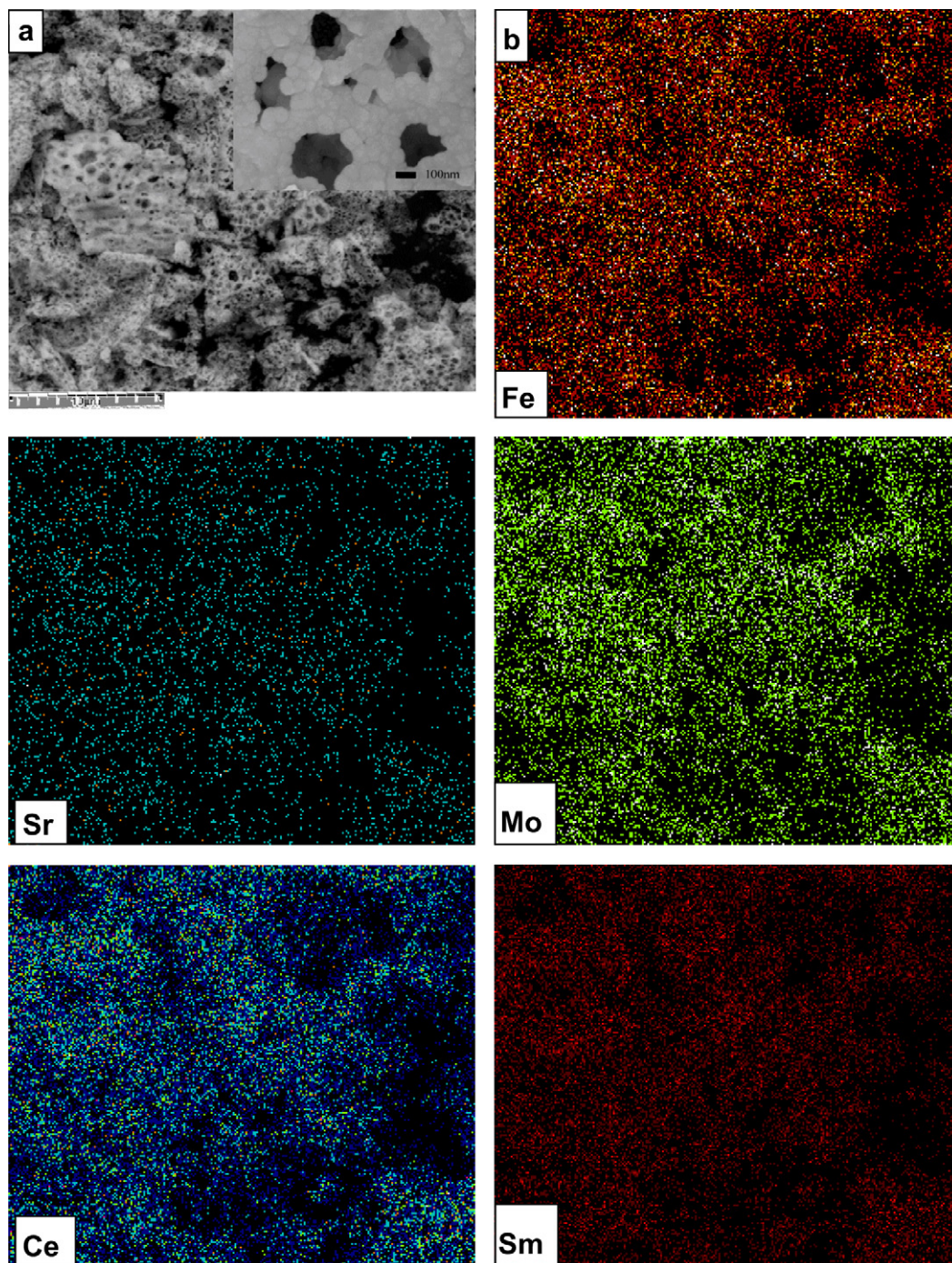


Fig. 2. (a) SEM image of the SFMO–SDC composite powders, (b) the corresponding EDX mapping of the composite powders.

temperature of 1000 °C for the cathode fabrication has no effect on the microstructure of this SFMO–SDC cathode. The size of the pores is estimated to be *ca.* 1 μm and the diameter of the nanoparticles is approximately 100 nm (Fig. 3b). Furthermore this resembles the microstructure of the powder (Fig. 2a). It is expected that such a microstructure which combines both a high-porosity scaffold and nanoparticles, will result in the enhancement of the TPB, which is itself essential to improve the overall electrochemical performance of the electrode. It is believed that a suitable microstructure may facilitate gas diffusion, electrochemical reaction, and electron and oxygen ion transport in the cathode [18,19]. Considering that a secondary phase might be formed between SFMO and YSZ after

firing at 1000 °C for 24 h in air [12], an SDC interlayer was introduced into the electrode structure within the single cell. This SDC layer is about 15 μm thick and is composed of interconnected SDC (Fig. 3a). Due to the appropriate TEC of the novel composite cathode ($14.3 \times 10^{-6} \text{ K}^{-1}$), the SFMO–SDC composite cathode exhibits good thermal compatibility with electrolyte/interlayer and no cracking was observed in the attached SDC interlayer.

3.2. Electrochemical performance

Fig. 4a shows the impedance spectra for the half cell of Pt/YSZ/SDC/SFMO-SDC. The difference between the intercepts of the

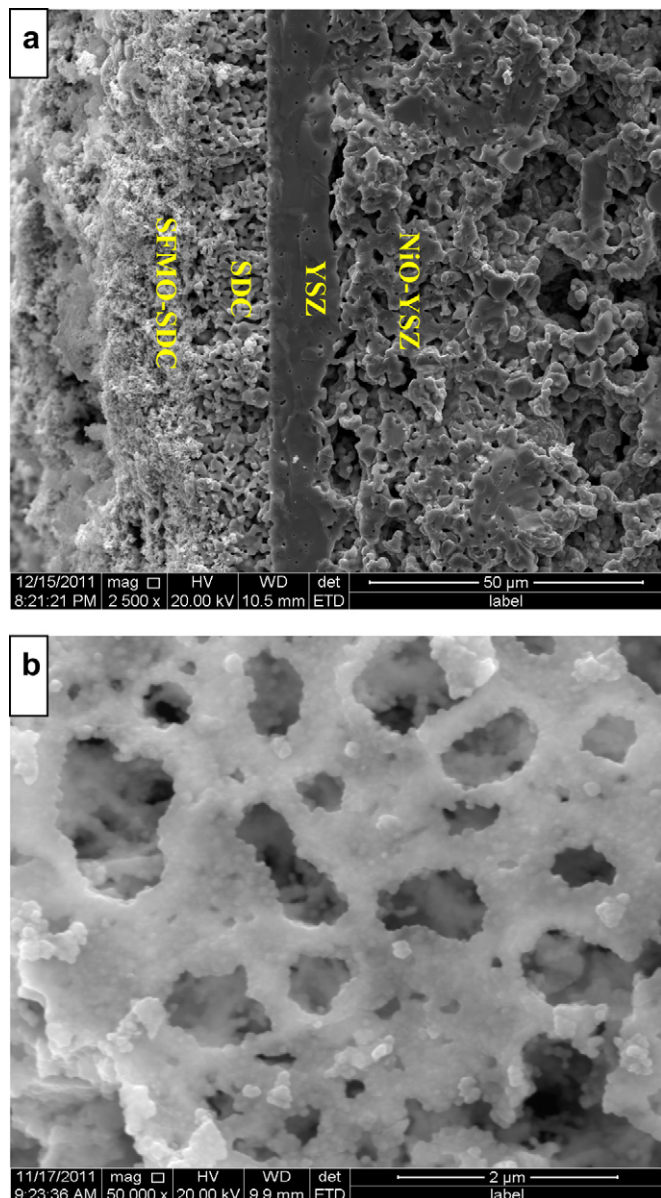


Fig. 3. SEM images of the tested cell with SFMO–SDC cathode: (a) the cross-section of the cell with SFMO–SDC cathode, (b) the surface of SFMO–SDC composite cathode.

impedance arc on the real axis relate to the polarization resistance of the cathode, denoted as area specific resistance (ASR). The ASR of the cathode measured through the three-electrode system were 0.16, 0.41 and $0.97 \Omega \text{ cm}^2$ at 800, 750 and 700°C , respectively, which is lower than that of the pure SFMO electrode ($0.24 \Omega \text{ cm}^2$ at 800°C based on an LSGM electrolyte) [12] and comparable to that of the nano-tube structured $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ –YSZ composite [20]. The low resistance should benefit from the SDC nanoparticles, which as previously discussed could accelerate the transport of oxygen ions through the electrode. Thus, considering that SDC and SFMO are homogeneously distributed in the porous microstructure, as shown in Fig. 3b, a high ORR activity for SFMO–SDC composite cathode could be achieved. To verify this, we investigated the electrochemical properties of the SFMO–SDC composite cathode by assembling a working fuel cell. Fig. 4b gives the I – V and I – P curves of the single cell based on the SFMO–SDC composite cathode. The maximum power densities of the fabricated single cell reach 2.21 , 1.66 , 1.16 and 0.71 W cm^{-2} at 800 , 750 , 700 and 650°C ,

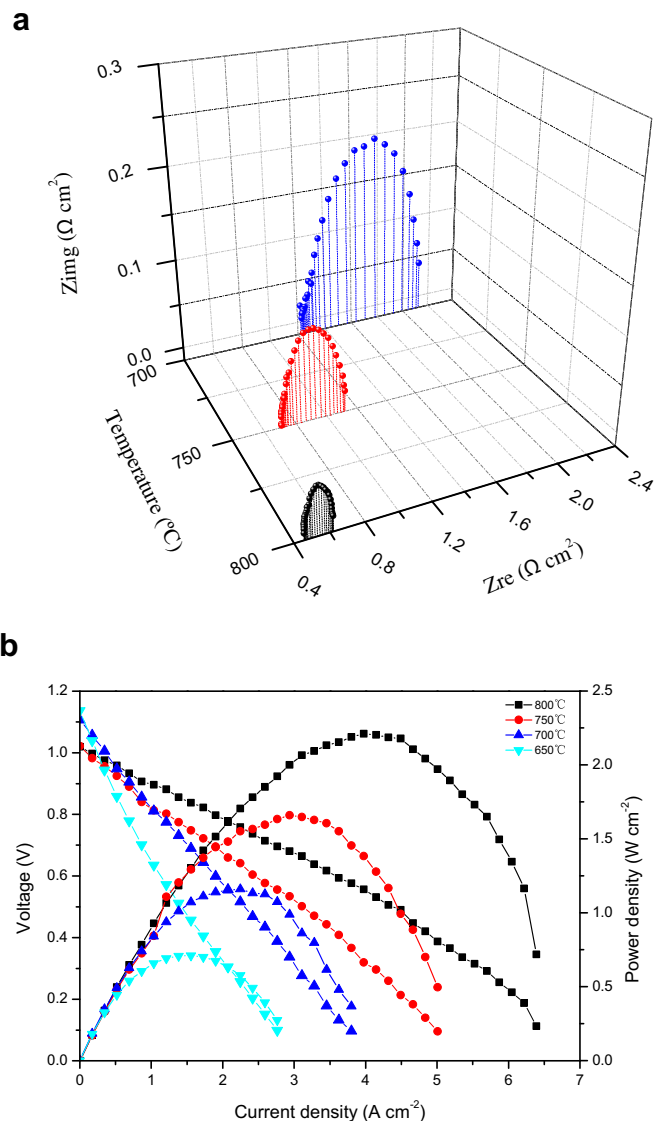


Fig. 4. (a) The EIS of the composite cathode of the Pt/YSZ/SDC/SFMO–SDC half-cell at 800 – 700°C in air, (b) I – V and I – P plots of the single cell with the composite cathode at 650 – 800°C .

respectively. Therefore the cell exhibits significant electrochemical performance over the temperature range of 650 – 800°C , indicating that SFMO–SDC is a promising composite cathode for application in IT-SOFCs. These remarkable power densities for the SFMO–SDC based single cell further confirm that the proposed one-step synthesis technology is an effective method of preparing the composite cathode with a suitable microstructure and performance for application in IT-SOFCs.

4. Conclusions

In this work, we have demonstrated a facile strategy to prepare SFMO–SDC composites for IT-SOFCs cathodes by a one-step self-combustion method. The resulting composite cathode contained uniformly distributed perovskite (SFMO) and fluorite-type structures (SDC). This proposed SFMO–SDC cathode was successfully assembled with a traditional YSZ electrolyte to fabricate an IT-SOFC utilizing NiO–YSZ as the anode. The SFMO–SDC composite based IT-SOFCs single cell achieved power densities of 2.21 , 1.66 and 1.16 W cm^{-2} at 800 , 750 and 700°C , respectively. Thus, the one-

step self-combustion method is an effective synthesis strategy to prepare promising SFMO–SDC composite cathode for IT-SOFCs. Moreover, it also provides a useful technique to prepare many other porous nanocomposite materials for various applications.

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